Effect of Thermal Aging on the Crystal Structural Characteristics of Poly(tetra fluoro ethylene)

Anjana Jain, Kalyani Vijayan
Materials Science Division, National Aerospace Laboratories, Bangalore 560 017, India

The residual effects of cumulative thermal aging on the crystal structural characteristics of the fluoro carbon poly(tetra fluoro ethylene) (PTFE) have been studied by X-ray diffraction methods. The initial hexagonal arrangement of the PTFE chains in a 15_7 helical conformation is left unaffected by the exposures to temperatures (T), up to and beyond its melting point, T_m. The unit cell registers a residual anisotropic volume expansion. The anisotropy arises from the enhanced enlargement of the basal plane dimension *a* compared with the axial dimension *c*. Conformational changes contributing to the observed increase in the chain length have been examined. Enhancement of residual crystallinity of samples aged at T's $< T_m$ suggests that the selective thermal aging could be used as an effective tool to improve the initial crystallinity of commercially available PTFE. The activation energy for 50% enhancement in initial crystallinity has been estimated as 53.9 kJ mol^{-1}. Aging at 400°C, a temperature above T_m, is accompanied by markedly different features viz., deterioration in crystallinity and other structural characteristics. The overall behavior of thermally aged PTFE bears a marked similarity to many polyamides. POLYM. ENG. SCI., 47:1724–1729, 2007. © 2007 Society of Plastics Engineers

INTRODUCTION

Study on the thermal aging behavior of polymeric materials has been a topic of interest [1–3] primarily because of the possible influence of such aging on their initial properties, subsequent behavior, and performance. In the past, the authors have carried out extensive investigations on the effects of thermal aging on some polyamides viz., Kevlar, Twaron, Nylon 6,6, and Nomex. Their studies established that the thermal aging causes significant residual effects on the crystal as well as macrostructural characteristics, tensile properties, weight, etc., of the polyamides [4–13]. This article reports the details of observations on the residual effects of thermal aging on the crystal structural characteristics of an entirely different type of polymer viz., a fluoro carbon, poly(tetra fluoro ethylene) (PTFE), derived by wide angle X-ray diffraction methods. The study also concerns deciphering similarities, if any, between the response of the fluoro carbon and the polyamides. Although PTFE is recommended for use at elevated temperatures up to 250–300°C, to date, data on the residual effects of thermal aging are not available. The work of Yamamoto and Hara [14] corresponds to X-ray data collected with an in situ heating arrangement, up to 250°C and does not concern residual effects. Residual effects are very important because structural changes, if any, left unnoticed, can affect the subsequent behavior of the material.

As this study concerns the structural characteristics, a brief account of the salient crystal structural characteristics of PTFE at various temperatures and other conditions, reported in literature, is included here. PTFE is known to undergo thermally induced structural transformations at ~19, 30, and 150°C, respectively [14–22]. The various thermally induced phases are characterized by helical conformations of chains with, however, distinct structural and helical features. At temperatures < 19°C, the PTFE molecule crystallizes in a triclinic/pseudohexagonal unit cell with a 13_6 helical conformation [15–19] and in the temperature range 19–30°C, a 15_7 helical conformation in a hexagonal unit cell has been observed [15, 16, 20, 21]. Farmer and Eby [22] predict a 54_{25} helix in a monoclinic unit cell for the former range of temperatures and the presence of both left- and right-handed helices in a triclinic unit cell for the latter range. Above 30°C, the 15_7 helix exhibits different types of disorders [15, 16, 21]. Close to 150°C, conformational changes in the 15_7 helix have also been reported [14]. Details of the structural characteristics of various phases, induced by thermal, mechanical, and pressure effects, have been compiled by Biswas and Vijayan [23]. These data indicate that the helical and the crystal structural characteristics of PTFE are indeed sensitive to thermal as well as mechanical treatments.

EXPERIMENTAL

The samples used in this study were procured commercially. Table 1 lists the temperatures at which the thermal

Correspondence to: Anjana Jain; e-mail: janjana@ccs.nal.res.in or janjana1@yahoo.com
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TABLE 1. T and t_{cum} (T) values chosen for analysis.

T (°C)	t_{cum} (T), h
150	100, 400, 700, 1000, 1500, 2000, 4000
250	50, 100, 350, 500, 850, 1150
300	200, 400, 550, 650
400	100, 200, 300

aging was conducted and the corresponding durations of cumulative exposures, t_{cum} (T). As could be appreciated, all the temperatures chosen were above the glass transition temperature, T_g, of PTFE viz., 127°C [24]. Although the melting point (T_m) of PTFE is 327°C, it has been mentioned that it degrades slowly only at T's above 400°C [24]. In this context, it was of interest to study the effect of excursions to 400°C, a temperature well above the T_m of PTFE.

Rectangular discs of approximate dimensions 16 × 13 × 2 mm^3 were heat-treated in air using a tubular resistance furnace with temperature control and stability of ±2°C. Temperatures were measured with a chromel–alumel thermocouple placed very close to the sample. For each of the chosen temperatures listed in Table 1, a separate disc was used for the progressive thermal aging. For T's $< T_m$, the discs were placed inside a quartz tube of diameter ~20 mm and slid into the furnace. At 400°C, however, the samples were found to soften and consequently the initially flat-surfaced discs acquired the curvature of the quartz tube in which they were encased. To avoid the introduction of such geometric changes, at 400°C, the discs were placed in a flat-bedded silica boat and slid into the furnace. It must be mentioned that at 400°C, a temperature well above the melting point, the PTFE discs could comfortably withstand a cumulative 300 h of exposure. Although immediately after the thermal exposures, the discs had a soft, jellylike appearance, they had not deformed physically and could be handled for subsequent recording of the X-ray patterns.

Prior to and at various stages of heat treatment, X-ray diffraction patterns were recorded in the 2θ range 13°–77° in the reflection geometry, using a Philips powder diffractometer and Cu Kα radiation. A graphite monochromater in the diffracted beam and a proportionate counter were used. Samples were rotated at the rate of ¼° per minute and the chart speed was 10 mm/min. In each set corresponding to a fixed temperature, patterns were recorded under identical experimental conditions and are therefore directly comparable.

The parameters estimated from the diffraction patterns were $2\theta_{max}$, half width (ω), and integrated intensities (I) of reflections. The mid-point chord extrapolation method [25] was used to estimate the $2\theta_{max}$ values. The unit-cell dimensions a and c were calculated by least squares method using the $2\theta_{max}$ values of six observed reflections, viz., (10.0), (11.0), (10.7), (10.8), (21.0), and (00.15). The indexing of reflections shown in Fig. 1 is based on the hexagonal unit cell reported earlier for PTFE [15, 16]. As the reflections (20.0) and (10.15) were too weak, the reliability in the estimation of the $2\theta_{max}$ values was low and hence these reflections were not included in the least squares calculations. Half-width values were measured manually using a scale. Integrated intensities were determined from the area under the diffraction profiles using a digitizer and an Autocad system. Using the direct correlation between total integrated intensity and crystallinity, the parameter $k = I_t(T)/I_o$ has been used to estimate the residual crystallinity of the sample [26]. Here, I_o and I_t (T) refer to the total integrated intensity in the X-ray diffraction patterns recorded from samples prior to and after heat treatment, respectively. It must be mentioned that in the 2θ range of 34°–44°, the reflections (20.0), (10.7), and (10.8) occur with slight overlap. As the analysis was concerned only with the relative variations in intensities/crystallinity, no attempt was made to remove the overlap. Densities of the as received and heat-treated discs were also estimated from the respective weight and volume values.

RESULTS AND DISCUSSION

Figure 1 compares some of the patterns from samples aged at 150°C with that recorded prior to the heat treatment. For the sake of convenience, only selected regions of the pattern, in the vicinity of the diffraction peaks, have been shown. The overall features seen in Fig. 1 are typical of patterns recorded from samples aged at other temperatures also. Occurrence of reflections at nearly the same 2θ values, both prior to and after heat treatment suggests that the initial hexagonal crystal structure is left

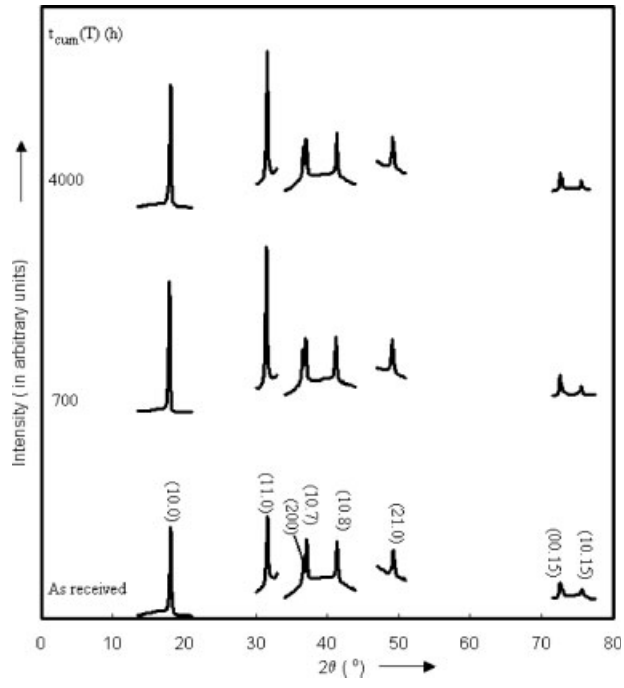

FIG. 1. X-ray diffraction profiles from PTFE prior to and after exposure to 150 °C. Values of (*hkl*) have been marked in one of the patterns.

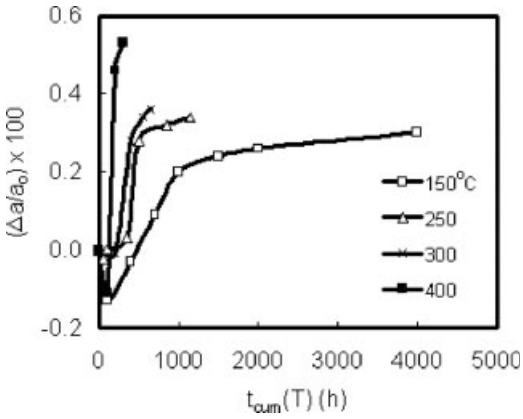

FIG. 2. Percentage variation in the a-value with T and $t_{cum}(T)$ values.

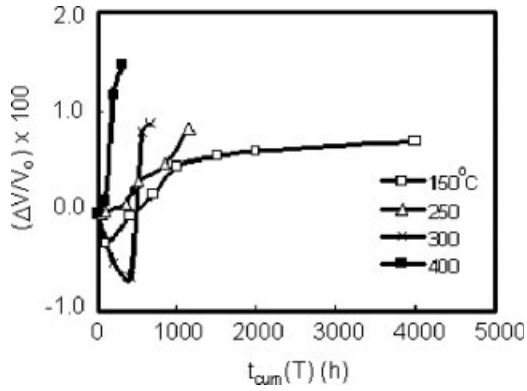

FIG. 4. Percentage variation in the unit-cell volume, V with T and $t_{cum}(T)$ values.

grossly unaffected by thermal exposures. Despite the overall similarity, the patterns from the heat-treated samples manifest subtle differences. In particular, the $2\theta_{max}$, intensity and half width values of reflections from heat-treated samples manifest small but detectable changes, the details and implications of which are described below.

Unit-Cell Parameters

For the samples used in this study, the unit-cell dimensions a and c, as estimated from five different specimens, prior to heat treatment, are 5.653(3) and 19.518(5) Å, respectively. These parameters compare well with the values $a = b = 5.61$, $c = 19.5$ Å [15] and $a = b = 5.66$, $c = 19.5$ Å [16] reported in literature. Figures 2–4 present the percentage variations in the unit-cell dimensions resulting from thermal aging, estimated as $(\Delta a/a_o) \times 100$, $(\Delta c/c_o) \times 100$, and $(\Delta V/V_o) \times 100$, respectively. Here, the suffix o denotes the parameters prior to heat treatment and $a(T)$, etc., correspond to the parameters of samples exposed to temperature T. The Δ's represent the differences of the type $a(T) - a_o$. Values of the estimated standard deviations (σ's) for the least squares refined unit-cell parameters a and c range from 0.001 to 0.01 Å, respectively, for samples both prior to and after heat treatment.

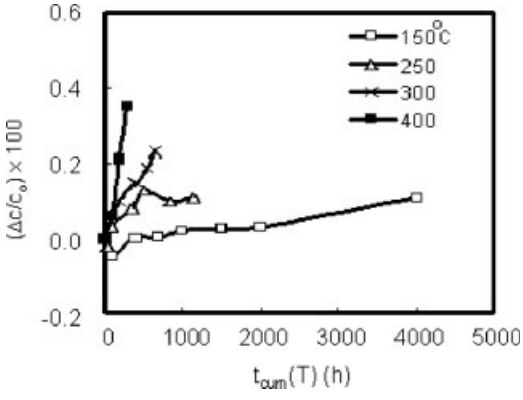

FIG. 3. Percentage variation in the c-value with T and t_{cum} (T) values.

Examination of the data in Figs. 2–4 shows that at each of the chosen T's, the first thermal exposure is accompanied by a reduction in the unit-cell parameters and a subsequent increase. From Fig. 4, it may be appreciated that the initial reduction in volume could be much as 0.7% (at 300°C). Such an initial reduction suggests that the first thermal exposure leads to an improved packing of the PTFE chains in the unit cell. Similar contraction of the unit cell was observed in the very early stages of sliding wear of PTFE and was attributed to improved packing of the chains in the unit cell [23, 27, 28]. The shrinkage suggests that the as-received PTFE samples perhaps include inherent structural defects or strain such as molecular misalignment and less efficient packing in the unit cell, which get relieved subsequently when the external energy is supplied. In the case of wear, the energy supplied to relieve the strain was mechanical in nature and in the present case, it is thermal.

The changes in the a-, c-, and V-values depend on the parameters T as well as t_{cum} (T). For a fixed value of T, increase in the t_{cum} (T) value introduces enhancements similar to that introduced by increase in T itself. It is also observed that for all the exposures chosen, the largest increase in the a- and c-values is <0.5%, a value which can be described, per se, as rather small. However, Table 2 shows that most of the observed shifts are $\geq 2\sigma$, thereby suggesting that the observed increments, though small,

TABLE 2. Typical $|\Delta l|/\sigma$ values for the least squares refined unit cell parameters.

T (°C)	$t_{cum}(T)$, h	$\lvert\Delta a\rvert/\sigma(\Delta a)$	$\lvert\Delta c\rvert/\sigma(\Delta c)$
150	100	3.25	2.77
	1500	4.50	2.90
	4000	4.10	3.26
250	500	3.82	3.23
	850	2.47	2.40
300	200	3.97	3.61
	400	5.49	4.15
400	200	2.67	2.65
	300	2.25	3.09

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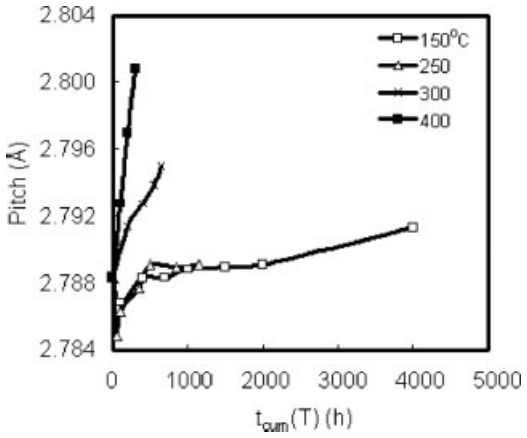

FIG. 5. Thermally induced variations in the pitch of the 15_7 helix with T and $t_{cum}(T)$.

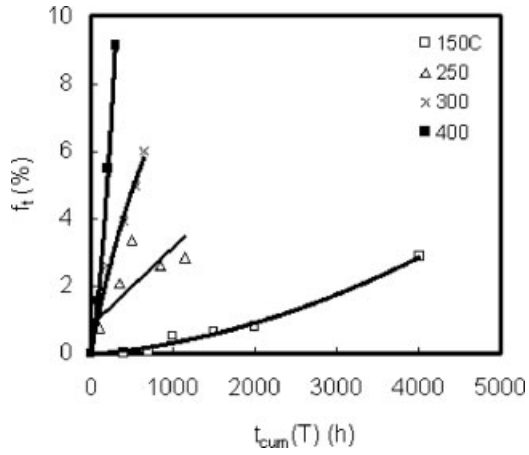

FIG. 7. Variation in the fraction in trans conformation, f_t, with T and $t_{cum}(T)$ values.

are statistically significant. The residual effect of thermal aging on the unit-cell parameters, though small, is statistically significant. It may also be pointed out that the residual changes manifested by samples aged at 400°C are conspicuously similar to those observed at T's $< T_m$ viz., the a-, c-, and V-values manifest an initial drop followed by a progressive increase.

Thermal aging leads to an anisotropic deformation of the unit cell. At any stage of thermal aging, the expansion in the basal plane dimension a is nearly 1.5–3 times more than the corresponding increase in the c-axial dimension. In the crystal structure of PTFE, the a-dimension refers to the interchain distance. The observed increase in the a-value may therefore be associated with a residual radial expansion of the helix, induced by thermal exposures. The c-length of the hexagonal unit cell is closely related to the helical characteristics, pitch, and rise per residue. From the observed c-values, progressive increase in pitch and rise per residue has been estimated (Figs. 5 and 6). It is found that at any T, increase in exposure time is accompanied by a slight "stretching" of the helix. Near overlap of the curves corresponding to 150 and 250°C and the distinctly higher values of pitch and rise per residue at 300 and 400°C, respectively, suggest that the helical dimensions are perhaps sensitive to a threshold temperature, which in this case appears to be between 250 and 300°C. With the retention of the 15_7 helix, the parameters' residue per turn and unit twist is, however, left unaffected by thermal exposures.

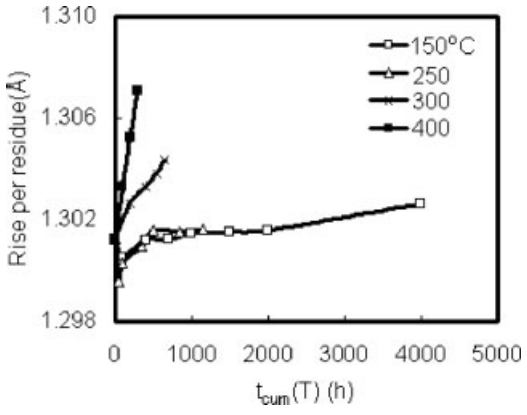

FIG. 6. Thermally induced variations in the rise per residue of the 15_7 helix with T and $t_{cum}(T)$.

The observed increase in the c-values has also been examined in the light of possible, localized, conformational changes. For a fictitious, all-trans conformation of the PTFE chain, the c-length of the unit cell is expected to be 20.25 Å. This dimension has been obtained by replacing the hydrogen atoms in the fully extended all-trans structure of polyethylene [15], which is the hydrocarbon analog of PTFE, by F atoms. Using 19.5 and 20.25 Å as the c-values representing the two extremes of conformations viz., purely helical and purely all-trans conformations, the fraction f_t of the chain, existing in a trans conformation has been interpolated for all the c-values representing thermally aged PTFE (Fig. 7). It is observed that after 300 h of exposure to 400°C, ~9% of the chain can exist in a trans conformation. The fraction f_t increases with T as well as $t_{cum}(T)$ values. The present study cannot distinguish between the two possible causes, which can lead to the observed increments in c-values viz., thermal expansion of the axial, helical dimension, and the introduction of partial conformational changes. It is not unlikely that both the effects are introduced to varying degrees in heat-treated PTFE.

Intensities

Interestingly, the total integrated intensity (I) in the diffraction patterns exhibits a progressive increase with thermal exposures. Such an overall increase in intensity suggests a corresponding increase in the crystallinity of the sample. The variation of residual crystallinity, k, estimated from the intensities of all the observed reflections

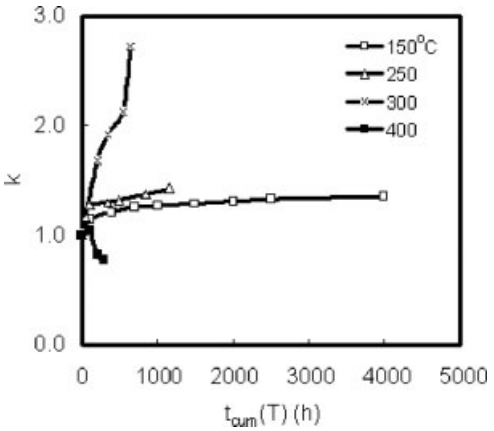

FIG. 8. Variation of residual crystallinity k with T and $t_{cum}(T)$ values.

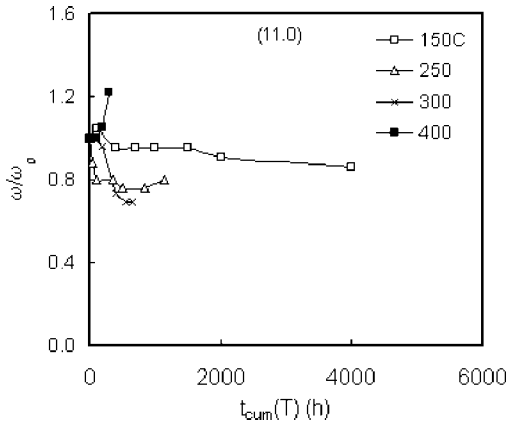

FIG. 9. Fractional variation in the half width value of the reflection (11.0) with T and $t_{cum}(T)$ values.

in the diffraction patterns is presented in Fig. 8. It is found that the increase in T as well as $t_{cum}(T)$ values leads to the enhancement in the k value. To quantify further, individual exposures of 4000 h at 150°C, 1150 h at 250°C, and 650 h at 300°C, respectively, lead to the corresponding improvements by 1.35, 1.42, and 2.7 times the initial crystallinity. Density values listed in Table 3 provide further evidence for the improvement in crystallinity at T's $< T_m$. These observations suggest that by a judicious choice of temperature and time, thermal aging can be advantageously utilized to improve the initial crystallinity of commercially available PTFE samples. From the observed increase in integrated intensity, the time needed for 50% increase in the initial crystallinity at various temperatures and the corresponding reaction rates, r, have been derived. From the slope of an Arrhenius plot, the activation energy for introducing 50% increase in the initial crystallinity has been estimated as 53.9 kJ mol^{-1}.

The variation in the crystallinity of samples exposed to 400°C is different from the changes observed at T's $< T_m$. Prolonged exposure to 400°C leads to the progressive reduction in the residual crystallinity (Fig. 8). Such a reduction is not very surprising, because we are considering excursions to a temperature well above the T_m of the material. The reduction in X-ray crystallinity observed at 400°C could be correlated with the onset of degradation at that temperature. It has been reported that PTFE degrades progressively at T's $>$ 400°C [24]. This study, however, suggests that degradation initiates, perhaps at 400°C itself. Thus, in contrast with the behavior at T's $< T_m$, aging at 400°C does not offer an advantageous tool for increasing the initial crystallinity of PTFE.

TABLE 3. Fractional values of density, ρ/ρ_o, at various temperatures.

T (°C)	$t_{cum}(T)$, h	ρ/ρ_o
23		1.00
150	4000	1.04
250	1150	1.08
300	650	1.12

ρ_o refers to the density value, 2050 Kg/m^3, prior to heat treatment.

It must be mentioned that the behavior of intensities in Yamamoto and Hara's in situ heating experiments [14] on PTFE fibers was very different from what has been observed in this study. According to the former's data, the intensity of the basal plane reflection (10.0) showed little change with temperature and in contrast, the intensities of the reflections (00.15) and (10.15) decreased rapidly and also accompanied by diffuse streaking along the 15th layer line. In this study, there was no evidence for the introduction of either diffuse streaking or decrease in intensity. The major difference between the two sets of experiments is that Yamamoto and Hara's data pertain to in situ heating conditions, whereas the present analysis corresponds to the residual effects of heating. Both seem to lead to distinctly different behaviors.

Half Width

The half widths (ω) of reflections recorded from samples heat treated at T's $< T_m$ manifest sharpening. Figure 9 presents a typical variation. As is well known, sharpening is an indication of increase in crystallite dimension and/or reduction in microstrain [29]. The behavior of reflections from samples aged at 400°C is, however, different. Here, the reflections manifest a broadening suggesting a corresponding reduction in crystallite size and/or build up of microstrain. This study thus suggests that the major changes, which could be considered as structural signatures for the onset of "degradation" at 400°C, are (i) reduction in crystallinity and (ii) introduction of microstrain and/or fragmentation of crystallites. These changes increase progressively with the $t_{cum}(T)$ values.

At this juncture, it must be pointed out that the overall nature of the changes introduced in the X-ray diffraction patterns from thermally aged PTFE viz., shifts in the 2θ values, changes in the intensities, half width, etc., are similar to those found in the polyamides mentioned earlier [4–13]. On the basis of the similarities, it may be

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surmised that the residual effect of thermal aging on the crystal structural characteristics is not exclusive to polyamides. A close comparison of data, however, shows that despite the overall similarities, the extent and direction of the shifts vary from polymer to polymer.

CONCLUSIONS

Thermal aging of PTFE introduces residual changes in crystal structural characteristics. Aging at both T's $< T_m$ and $T > T_m$ have a similar influence on the unit-cell parameters viz., at each T, an initial reduction followed by a subsequent progressive increase with aging time is registered. It appears that after completing the thermal exposures, the initial hexagonal cell is left in a slightly expanded state like a memory effect of the thermal expansion, which would have occurred during the respective thermal exposures. The residual expansion of the unit cell is anisotropic. The basal plane dimension a expands more than the c-axial length. Exposures to T's $< T_m$ cause an enhancement in the intensities suggesting an improvement in the initial crystallinity of the sample. This observation suggests that the thermal aging at selected temperatures for appropriate time durations could be used as an effective tool to improve the crystallinity of commercially available PTFE. The activation energy for 50% increase in the initial crystallinity is estimated to be 53.9 kJ mol^{-1}. Sharpening of reflections accompanying exposures suggests thermally induced growth of crystallites and/or reduction in microstrains. PTFE manifests an overall similarity to polyamides in its response to exposures to T's $< T_m$. Exposures to 400°C cause reduction in crystallinity and also broadening of reflections. These features could be treated as structural signatures of the onset of thermally induced degradation initiating at 400°C. All the structural changes manifest a dependence on T as well as $t_{cum}(T)$ values.

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